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INVERSION FOR MASS SPECTROMETER MULTICOMPONENT SAMPLING

Christopher Sherman

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A mass spectrometer samples a neutral gas consisting of more than one component. During sampling, the component species are not only ionized, but also fragmented, thus introducing mass fragments not present in the original gas. A method has been developed that uses the resultant measured spectral intensity ratios to find the density or partial pressure ratios of the original components. In addition to spectral intensity ratios, the following is assumed to be known: the fragments produced from each original component; the branching ratios of these fragments; and the ratios of ionization efficiencies for each component pair. Since this method depends only on spectral and ionization *ratios*, it is in principle (although in practice, not completely) independent of the variable, and often time dependent, characteristics of individual instruments.

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Inversion for Mass Spectrometer Multicomponent Sampling

1. INTRODUCTION

This report addresses the problem of a mass spectrometer sampling a neutral gas consisting of more than one component. During sampling, the component species are not only ionized, but also fragmented, thus indroducing mass fragments not present in the original gas. We want to use the resultant spectral intensity ratios to find the density or partial pressure ratios of the original components. In addition to the spectral intensity ratios, the following are assumed to be known: the fragments produced from each original component; the branching ratios of each of these fragments; and the ratios of ionization efficiencies for each component. In principle, all the known quantities are independent of particular mass spectrometer characteristics, such as multiplier gain for example, so that the procedure need not take into account the peculiarities of a specific instrument. It is required, however that the branching ratios and hence the electron beam energies be the same for both branching ratio and sample measurements.

Note the frequent reference to *ratios* of values rather than values per se. This is because many of these values vary from instrument to instrument, and further, for any given instrument, with time. As noted, we are seeking an inversion that is independent of instrument properties, such as ion source characteristics or multiplier gain. If these properties

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are assumed to remain fixed, then inversion is quite simple. If they are not fixed, then the method described here, a more complicated procedure, or possibly some other procedure must be resorted to.

2. GENERAL SOLUTION OF THE PROBLEM

Let C_j be the density or partial pressure of the neutral compounds, m in number, j=1 to m.

Let α_j be the ionization efficiency of the jth component.

Let the B_{ij} be the spectral intensities of the ith fragment of the jth compound. This will be an array of n rows (i runs from 1 to n) and m columns (j runs from 1 to m). The rows identify fragments of a given mass (including in particular, the mass of the unfragmented ion); the columns identify a given input component.

Let I=I (j) index the mass of the jth unfragmented component, so that B_{Ij} when I is written without an argument is a one dimensional array, dependent on j only. $B_{I(\ell)J}$, however (I(ℓ) written *with* an argument) is once again a member of a two dimensional array, with subscripts I(ℓ) and j.

At this point, to clarify the notation, we illustrate by displaying a specific example. For this purpose we choose a gas having four components: CO, CO_2, $C_2H_4O_2$, and O_2, and assume that the first two and last of these, but not the third, is decomposed into every possible fragment. Let the compounds be sequenced in the order given above. Then, the array for the B_{ij} looks as follows. (M is the fragment mass number).

Table 1. Illustrative Table of Symbolic Values for B_{ij}.

M \ C_j	C_1 (CO)	C_2 (CO_2)	C_3 ($C_2H_4O_2$)	C_4 (O_2)
12	B_{11}	B_{12}	B_{13}	$B_{14} = 0$
16	B_{21}	B_{22}	B_{23}	B_{24}
28	B_{31}	B_{32}	B_{33}	$B_{34} = 0$
32	$B_{41} = 0$	B_{42}	B_{43}	B_{44}
44	$B_{51} = 0$	B_{52}	B_{53}	$B_{54} = 0$
60	$B_{61} = 0$	$B_{62} = 0$	B_{63}	$B_{64} = 0$

In general, most of the B_{ij} will be zero, but for this relatively small system they are not. We have, m = 4, n = 6, and I(1) = 3: I(2) = 5: I(3) = 6: I(4) = 4.

This example will be used again in Section 3 to demonstrate a sample solution.

Returning now to the general development, we have the component conservation relations

$$\alpha_1 C_1 = \sum_{i=1}^{n} B_{i1} \tag{1a}$$

$$\alpha_2 C_2 = \sum_{i=1}^{n} B_{i2} \tag{1b}$$

$$\vdots$$

$$\alpha_j C_j = \sum_{i=1}^{n} B_{ij} \tag{1c}$$

$$\vdots$$

$$\alpha_m C_m = \sum_{i=1}^{n} B_{im} \tag{1d}$$

Let $\rho_{ij} = \frac{B_{ij}}{B_{Ij}}$ and $\beta_j = \frac{\alpha_{j+1}}{\alpha_j}$. The ρ_{ij} are relative branching ratios, and the β_j the ionization efficiency ratios referred to in the introduction.

Let $y_j = \frac{C_j}{C_{j+1}}$

Then

$$y_1 = \beta_1 \sum_{i=1}^{n} B_{i1} / \sum_{i=1}^{n} B_{i2} = \beta_1 \frac{B_{I1}}{B_{I2}} \sum_{i=1}^{n} \rho_{i1} / \sum_{i=1}^{n} \rho_{i2} \qquad (2a)$$

$$y_2 = \beta_2 \sum_{i=1}^{n} B_{i2} / \sum_{i=1}^{n} B_{i3} = \beta_2 \frac{B_{I2}}{B_{I3}} \sum_{i=1}^{n} \rho_{i2} / \sum_{i=1}^{n} \rho_{i3} \qquad (2b)$$

$$\vdots$$

$$y_j = \beta_j \sum_{i=1}^{n} B_{ij} / \sum_{i=1}^{n} B_{i,j+1} = \beta_j \frac{B_{Ij}}{B_{I,j+1}} \sum_{i=1}^{n} \rho_{ij} / \sum_{i=1}^{n} \rho_{i,j+1} \qquad (2c)$$

$$\vdots$$

$$y_{m-1} = \beta_{m-1} \sum_{i=1}^{n} B_{i,m-1} / \sum_{i=1}^{n} B_{im} = \beta_{m-1} \frac{B_{I,m-1}}{B_{Im}} \sum_{i=1}^{n} \rho_{i,m-1} / \sum_{i=1}^{n} \rho_{im} \qquad (2d)$$

Let $B_{Ij}/B_{I,j+1} = x_j$: $j = 1$ to $m - 1$: $x_m = 1$

and $\sum_{i=1}^{n} \rho_{ij} / \sum_{i=1}^{n} \rho_{i,j+1} = S_j$.

Then $y_1 = \beta_1 x_1 S_1$

$$y_2 = \beta_2 x_2 S_2$$

$$\vdots$$

$$y_k = \beta_k x_k S_k \qquad (3)$$

$$\vdots$$

$$y_{m-1} = \beta_{m-1} x_{m-1} S_{m-1}$$

The reason for the condensation of notation is that all β_k and S_k are known. We now need to obtain the x_k to complete the solution.

Let $\Omega_1 = \sum_{j=1}^{m} B_{I(1)j} / \sum_{j=1}^{m} B_{I(2)j}$

$$\Omega_2 = \sum_{j=1}^{m} B_{I(2)j} / \sum_{j=1}^{m} B_{I(3)j}$$

$$\vdots$$

$$\Omega_k = \sum_{j=1}^{m} B_{I(k)j} / \sum_{j=1}^{m} B_{I(k+1)j}$$

$$\vdots$$

$$\Omega_{m-1} = \sum_{j=1}^{m} B_{I(m-1)j} / \sum_{j=1}^{m} B_{I(m)j}$$

The Ω_k are the intensity ratios of the MEASURED SPECTRAL LINES, having the masses of the unfragmented input compounds. We now show that the right hand sides of the expressions for Ω_k can be expressed in terms of the ρ_{ij} and x_k. Since the Ω_k are m-1 in number these then constitute a closed set of simultaneous implicit equations for x_k. When solved for the x_k they give us the solutions for the required values of y_k.

We could just as easily have selected any other of the (m-1)! sets of spectral ratios formable from the intensities of the m unfragmented species. However, the choice made is readily identifiable and seems a natural choice. The manipulation of the expressions for Ω_k to put them in terms of ρ_{ij} and x_k will be done for k = 1. The other relations then follow by augmentation of the k index.

$$\Omega_1 = \frac{B_{I(1)1} + B_{I(1)2} + \ldots B_{I(1)j} + \ldots B_{I(1)m}}{B_{I(2)1} + B_{I(2)2} + \ldots B_{I(2)j} + \ldots B_{I(2)m}} \qquad (4a)$$

$$= \frac{B_{I1} + B_{I2}\,\rho_{I(1)2} + \ldots B_{Ij}\,\rho_{I(1)j} + \ldots B_{Im}\,\rho_{I(1)m}}{B_{I1}\,\rho_{I(2)1} + B_{I2} + \ldots B_{Ij}\,\rho_{I(2)j} + \ldots B_{Im}\,\rho_{I(2)m}} \qquad (4b)$$

Note in the subscripts of B, the switch from argumented I (I(1), I(2)) in Eq. (4a) to UNARGUMENTED I in Eq. (4b). This is preparatory to expressing ratios of B_{Ij} in terms of x_j. Next, divide numerator and denominator by B_{Im} and observe that

$$B_{Ij}/B_{Im} = x_j x_{j+1} \cdots x_{m-1} = \prod_{i=j}^{m-1} x_i \tag{5}$$

so that

$$\Omega_1 = \sum_{j=1}^{m} \rho_{I(1)j} \prod_{i=j}^{m} x_i / \sum_{j=1}^{m} \rho_{I(2)j} \prod_{i=j}^{m} x_i. \tag{6a}$$

(In these as well as the remaining sums, we have

$$\rho_{I(1)1} = \rho_{I(2)2} = \cdots \rho_{I(j)j} = \cdots \rho_{I(m-1),m-1} = 1).$$

In like manner,

$$\Omega_2 = \sum_{j=1}^{m} \rho_{I(2)j} \prod_{i=j}^{m} x_i / \sum_{j=1}^{m} \rho_{I(3)j} \prod_{i=j}^{m} x_i \tag{6b}$$

$$\vdots$$

$$\Omega_k = \sum_{j=1}^{m} \rho_{I(k)j} \prod_{i=j}^{m} x_i / \sum_{j=1}^{m} \rho_{I(k+1)j} \prod_{i=j}^{m} x_i \tag{6c}$$

$$\vdots$$

$$\Omega_{m-1} = \sum_{j=1}^{m} \rho_{I(m-1)j} \prod_{i=j}^{m} x_i / \sum_{j=1}^{m} \rho_{I(m)j} \prod_{i=j}^{m} x_i \tag{6d}$$

Let $z_j = \prod_{i=j}^{m} x_i$: $1 \le j \le m$.

Then, clearing the kth equation of fractions

$$\Omega_k \sum_{j=1}^{m} \rho_{I(k+1)j}\, z_j = \sum_{j=1}^{m} \rho_{I(k)j}\, z_j. \tag{7}$$

Let $A_{jk} = \Omega_k\, \rho_{I(k+1)j} - \rho_{I(k)j}$.
Then

$$\sum_{j=1}^{m} A_{jk} z_j = 0 \qquad 1 \leqq k \leqq m\text{-}1 \tag{8}$$

form a set of m-1 linear equations for the m-1 unknowns z_j which can be solved by one of the usual methods. Following this, the x_j are recovered from

$$x_j = z_j / z_{j+1} \qquad 1 \leqq j \leqq m\text{-}1.$$

This completes the solution.

3. EXAMPLE

To illustrate these ideas, we first assign values to the array for the B_{ij} shown in Table 1 and also to the required values of α_j the ionization efficiencies. Here, the units for the values of B_{ij} (the spectral intensities of the ith mass fragment from the jth compound) may be taken as microamperes; and those for the ionization efficiencies, when normalized to a pressure of one Torr, as microamperes per Torr. Note that the column sum of spectral intensities is set equal to the corresponding value of α_j. This assignment is somewhat arbitrary. Strictly, the sum of the branching ratios for each component is unity, and dividing each value of B_{ij} by α_j will yield this result. If the B_{ij} are the actual fragment spectral intensities due to an arbitrary mixture of gases, neither of these is true; each column will be multiplied by an (unknown) constant, dependent on the partial pressure of that particular component. Only with this assignment will Eq. (1) be true. These constant values however, are precisely those we are seeking with

this treatment, and so are not known. However, since all equations except Eq. (1) deal only with RELATIVE values for all variables, the actual values as well as the units turn out to be of no import. Only the RELATIVE VALUES in each column are required. To the right of the array, are listed the intensities of the MEASURED mass spectrum. From these, will be formed the three (= m-1) values of Ω_k required for solution. We note that none of the values given here are actual measured values; those for CO, CO_2 and O_2 are reasonable, but all have been fabricated for purposes of illustrating the method of solution.

Table 2. Values of B_{ij}.

M \ C_j	C_1 (CO)	C_2 (CO_2)	C_3 ($C_2H_4O_2$)	C_4 (O_2)	Measured Spectral Intensities
12	0.0025	0.0009	0.005	0	0.002
16	0.05	0.03	0.01	0.15	0.2
28	0.5	0.06	0.02	0	0.4
32	0	0.0009	0.005	1.5	1
44	0	0.3	0.02	0	1
60	0	0	0.2	0	2
α_i	0.5525	0.3919	0.260	1.65	

Next we form the table of the ρ_{ij} by dividing B_{ij}/B_{Ij}. We also form the Ω_j, and the β_j.

Table 3. Values of ρ_{ij}, Ω_j, and β_j.

M \ C	C_1 (CO)	C_2 (CO_2)	C_3 ($C_2H_4O_2$)	C_4 (O_2)	Ω
12	0.005	0.003	0.025	0	$\Omega_1 = 0.4/1 = 0.4$
16	0.1	0.1	0.05	0.1	
28	1.0	0.2	0.1	0	$\Omega_2 = 1/2 = 0.5$
32	0	0.003	0.025	1.0	
44	0	1.0	0.1	0	$\Omega_3 = 2/1 = 2.0$
60	0	0	1.0	0	
$\beta_1 = 0.709$		$\beta_2 = 0.663$		$\beta_3 = 6.35$	

From these,

$$S_1 = \frac{1.105}{1.360} = 0.8271; \qquad S_2 = \frac{1.360}{1.300} = 1.046; \qquad S_3 = \frac{1.300}{1.100} = 1.182$$

and

$$y_1 = 0.5864\, x_1; \qquad y_2 = 0.6935\, x_2; \qquad y_3 = 7.506\, x_3.$$

To complete the solution, we next form the equations for the x_k.

$$\Omega_1 = \frac{x_1x_2x_3 + 0.2x_2x_3 + 0.1x_3 + 0}{0 + x_2x_3 + 0.1x_3 + 0} = \frac{x_1x_2 + 0.2x_2 + 0.1}{x_2 + 0.1}$$

$$\Omega_2 = \frac{0 + x_2x_3 + 0.1x_3 + 0}{0 + 0 + x_3 + 0} = x_2 + 0.1$$

$$\Omega_3 = \frac{0 + 0 + x_3 + 0}{0 + 0.003x_2x_3 + 0.025x_3 + 1} = \frac{x_3}{0.003x_2x_3 + 0.025x_3 + 1}.$$

Here, the system is so simple we need not introduce the z_j; instead we find directly

$$x_1 = 0.05; \qquad x_2 = 0.40; \qquad x_3 = 2.111$$

and

$y_1 = [CO]/[CO_2] = 0.02932$

$y_2 = [CO_2]/[C_2H_4O_2] = 0.2774$

$y_3 = [C_2H_4O_2]/[O_2] = 15.84$

4. THE DEGENERATE CASE

It may turn out that two (or possibly more) of the unfragmented input compounds have identical masses. A good example of this would be the presence in the measured sample of CO_2 and N_2O. Since this only appears as a single peak in the measured spectrum, we would then seem not to have the required m-1 values of Ω_k needed to complete the solution. If however, the sum of the components is treated as a single component, we can still obtain, instead of the m-1, m-2 ratios of the input components, with the sum of the degenerate components appearing as a single component.

5. UNRESOLVED ISSUES

We have tacitly assumed that real, positive solutions for the x_k can always be found. This seems to be intuitively clear on the following grounds. If instead of inversion, we start from any known mixture, we will always produce a specific spectrum containing both unfragmented and fragmented spectral lines. Thus, when the process IS inverted, we know that a solution exists; it is reasonable to assume then, that this solution will be obtained. Still, such reasoning does not constitute a proof, and no proof has yet been found.

If this reasoning is correct however, we have here a means of checking on the quality of experimental data. If a solution cannot be found, then this indicates that there is an inconsistency between the spectra measured, the measured branch ratios, and the measured ionization efficiencies. One aspect of this question might be pursued further by investigating the way assumed errors in the measured spectra are propagated backward into the calculated original components.

Another question is whether it is possible by further work to find the ratio of input compounds even when they do have the same mass. This issue is not pursued further here.